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Stretton, Shropshire SY6 7AR (GB). MT JOY, Raymond [US/US]; 18511 Brackenfield Drive, Spring, TX 77388 (US).

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(74) Agent: STROZIER, Robert, W.; Robert W. Strozier, PLLC, P.O. Box 429, Bellaire, TX 77402-0429 (US).

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(71) Applicant (*for all designated States except US*): LOBO LIQUIDS, LLC [US/US]; 18937 Aldine-Westfield Road, Houston, TX 77073 (US).

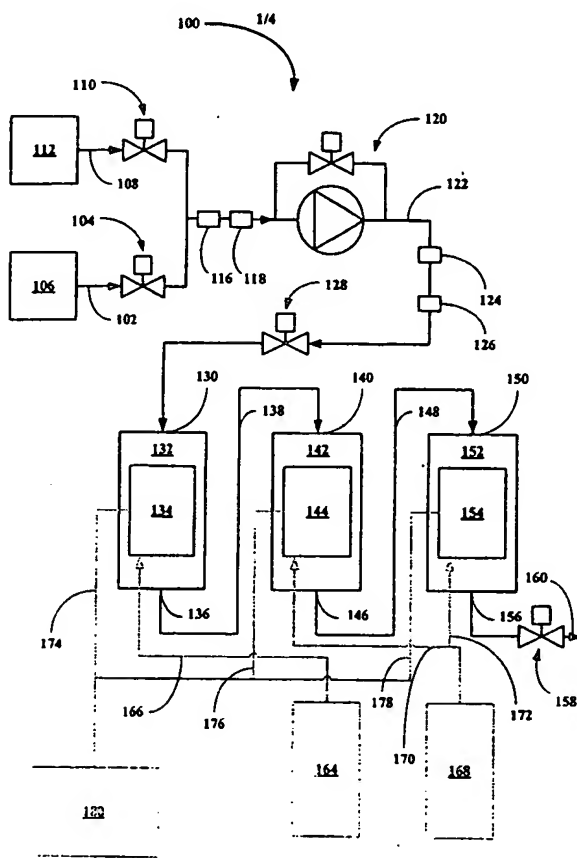
(72) Inventors; and

(75) Inventors/Applicants (*for US only*): TUNNICLIFFE, Ian [GB/GB]; Cotsdale, Watling Street North, Church

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[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR TREATING METAL ION CONTAINING STREAMS



(57) Abstract: A method for removing metal ions from aqueous streams is disclosed using an extraction system of this invention, which includes at least one and preferably a plurality of extraction units comprising a bed filled with a volumetric mixture of an ion exchange material and an inert material. Preferably, the mixture includes between about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material. The method is designed to operate at a relatively high stream flow rate, preferably between about 1.5 and about 5 times greater than the flow rate of the stream not equipped with the present extraction system.

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**PATENT SPECIFICATION**

TITLE: METHOD AND APPARATUS FOR TREATING METAL ION CONTAINING STREAMS

**RELATED APPLICATION**

[0001] This application claims provisional priority to United States Provisional Patent Application Serial No. 60/384,776 filed 30 May 2002.

**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0002] The present invention relates to a method for removing metal ions from a stream using a volumetrically diluted strong acid ion exchange resin at substantially increased stream flow rates and to apparatuses for performing the method.

[0003] More particularly, the present invention relates to a method for removing metal ions from aqueous streams contaminated with metal ions using a strong acid ion exchange resin volumetrically diluted with an inert material at substantially increased stream flow rates to achieve compliance with EPA clean water standards and apparatuses for performing the method. The method and apparatus are especially well-suited for closed loop systems where the cleaned water is reused in the industrial process, with only small quantities of new water being added on a routine or periodic basis.

**2. Description of the Related Art**

[0004] Current EPA clean water standards have greatly lowered acceptable limits of most metal ions in aqueous effluents from industrial and chemical processes. The lower limits are especially important for heavy metal such as transition metals and actinide metals and lanthanide metals. Many system exist extract or remove the metals by a variety of different methods. One popular method involves the use of ion exchange resin such as strong acid ion exchange resins, which generally includes a polymer backbone having sulfonic acid groups attached thereto or other strong mineral acid groups attached thereto.

[0005] Although many systems including home units for water softening utilize such resins, utilize strong acid ion exchange resins for removal of metal ion contaminated streams, there is a need in the art for an process that quickly and efficiently removes metal ion contaminants in water to level either below general analytical detection limits or at or below new EPA metal ion

concentration guidelines for compliance with the new clean water standards.

### **SUMMARY OF THE INVENTION**

[0006] The present invention provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one zone comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.

[0007] The present invention provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through a plurality of zones comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.

[0008] The present invention also provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one zone comprising a volumetric mixture of from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material at a relatively high stream flow rate, where the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industrial application. The stream flow rate generally used in industrial applications depends on the size and type of application and vary greatly; however, the present invention achieves metal ion removal at flow rates at least about 1.5 to about 5 times the standard flow rate, with higher and lower flow rates being possible depending on the application.

[0009] The present invention also provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through a plurality of zones, each zone comprising a volumetric mixture of from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material, where the stream passed through each zone at a relatively high stream flow rate, where the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industrial application.

[0010] The present invention provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.

[0011] The present invention provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through a plurality of beds comprising a volumetric mixture of an ion exchange material and an a substantially inert material

at a relatively high stream flow rate.

[0012] The present invention also provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one bed comprising a volumetric mixture of from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material at a relatively high stream flow rate, where the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industrial application.

[0013] The present invention also provides a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through a plurality of beds, each bed comprising a volumetric mixture of from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material, where the stream passed through each bed at a relatively high stream flow rate, where the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industrial application.

[0014] The present invention also provides a method for removing metal ions from aqueous streams contaminated with metal ions to form a aqueous stream having metal ion concentration at or below the concentrations dictated by the current clean water standards, where the method include the step of passing the stream through a bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate producing the desired aqueous output stream.

[0015] The present invention provides a method for closed loop circulation of aqueous stream with concurrent removal of metal ion contaminants contained in the stream, where the method includes the step of directing an effluent stream of an industrial process contaminated with metal ions to an extraction unit including at least one zone or bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material, passing the effluent stream through the zone or bed at a relatively high stream flow rate to produce a cleaned stream having metal ion concentrations at or below existing clean water standards, and directing the cleaned stream into an inlet of the industrial process. This process can either be done on a continuous basis or on a periodic basis depending on the exact nature of the industrial process, but it is preferably carried out on a continuous or sem-continuous basis.

[0016] The present invention provides a method for closed loop circulation of aqueous stream with concurrent removal of metal ion contaminants contained in the stream, where the method includes the step of directing an effluent stream of an industrial process contaminated with metal

ions to an extraction unit including at least one zone or bed comprising a volumetric mixture of from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material, passing the effluent stream through the zone or bed at a relatively high stream flow rate, where the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industrial application, to produce a cleaned stream having metal ion concentrations at or below existing clean water standards, and directing the cleaned stream into an inlet of the industrial process. This process can either be done on a continuous basis or on a periodic basis depending on the exact nature of the industrial process, but it is preferably carried out on a continuous or sem-continuous basis.

#### **Apparatuses for Carrying Out the Methods of This Invention**

[0017] The present invention provides an apparatus for removing metal ion contaminants from an effluent stream comprising an extraction unit including an inlet and an outlet and at least one bed or zone comprising a volumetric mixture of an ion exchange resin and an inert material. The apparatus also preferably includes a pump sufficient to increase the volumetric flow rate of the stream.

[0018] The present invention provides an apparatus for removing metal ion contaminants for a closed loop circulation of aqueous stream, where the apparatus includes an industrial application producing an effluent stream contaminated with metal ions and an extraction unit including at least one zone or bed comprising a volumetric mixture of an ion exchange material and from a substantially inert material, where the metal ion contaminants are removed to a desired low level to produce a clean recycle stream. The industrial application and the extraction unit are connected by an effluent line so that the effluent stream flows from the industrial application into the extraction unit on a continuous or periodic basis and a recycle line so that the clean recycle stream flows from the extraction unit into the industrial application. The apparatus also includes at least on pump in either the effluent line or the recycle line to increase the flow rate between about 1.5 and about 5 times greater than a standard flow rate for the industrial process.

#### **DESCRIPTION OF THE DRAWINGS**

[0019] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawings in which like elements are numbered the same:

[0020] Figure 1 depicts a schematic diagram of a preferred embodiment of the system of this invention;

[0021] Figure 2 depicts a schematic diagram of the system of Figure 1 indicating the test points

monitored during regeneration;

[0022] Figure 3 depicts a diagram Showing The Test Site Decorative Chromium Plating Line and Lobo Liquids Rinse Water Recycle System; and

[0023] Figure 4 depicts Specific Conductivity of System of this invention Effluent During ETV Test Period.

### **DETAILED DESCRIPTION OF THE INVENTION**

[0024] The inventors have found a high efficient and cost effective metal ion extraction system and methods based thereon can be constructed, where an effluent stream including metal ion contaminants is passed through at least one zone or bed comprising a volumetric mixture of an ion exchange material and a substantially inert material. By volumetrically diluting the ion exchange resin and increase a flow rate of the stream to be cleaned, the inventors have found that metal ions can be removed to at or below a given target value, where the target values are preferably at or below the current clean water concentrations.

[0025] The present invention relates broadly to a method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one zone or bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate. Preferably, the stream is passed through a plurality of beds, where the plurality is preferably between about 2 and about 10 bed. Preferably, the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material. Particularly, the volumetric mixture comprises from about 90 to 60 vol% of an ion exchange material and from about 10 to 40 vol% of an a substantially inert material. More particularly, the volumetric mixture comprises from about 90 to 70 vol% of an ion exchange material and from about 10 to 30 vol% of an a substantially inert material. However, other mixture can be used as well depending on the nature of the stream and the efficiency of the extraction wanted in each zone. Of course, the mixture can be the same or different in each bed, again depending on the removal efficiency desired for each zone or bed.

[0026] The present invention also relates broadly to a method for removing metal ions from closed looped industrial application, where effluent streams contaminated with metal ions are cleaned and returned on a periodic or continuous basis. The method includes the steps of directing effluent streams into an extraction unit including at least one zone or bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material. The effluent stream(s) is then passing through the at least one zone or bed at a relatively high stream

flow rate, where metal ions are removed from the stream. After a desired reduction in metal ion concentration in the effluent stream is achieved, the cleaned stream is directed back into the industrial application. Preferably, the stream is passed through a plurality of beds, where the plurality is preferably between about 2 and about 10 bed. Preferably, the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material. Particularly, the volumetric mixture comprises from about 90 to 60 vol% of an ion exchange material and from about 10 to 40 vol% of an a substantially inert material. More particularly, the volumetric mixture comprises from about 90 to 70 vol% of an ion exchange material and from about 10 to 30 vol% of an a substantially inert material. More specifically, the volumetric mixture comprises from about 85% to about 65% of an ion exchange material and from about 15 to about 35% of an inert material and optimally, from about 72% to about 70% of an ion exchange material and from about 28 to about 30% of an inert material. However, other mixture can be used as well depending on the nature of the stream and the efficiently of the extraction wanted in each zone. Of course, the mixture can be the same or different in each bed, again depending on the removal efficiency desired for each zone or bed.

[0027] Suitable ion exchange materials include, without limitations, ion exchange resins, ion exchange ceramics, or any other material having ion exchange activity. Preferably, the material are strong acid ion exchange materials. Preferred strong acid ion exchange resins include, without limitation, polymeric resins containing aromatic groups that have been treated with sulfuric acid and sulfonated. Particularly preferred strong acid ion exchange resins include, without limitation, polystyrene/divinylbenzene resin in traditional or macroreticular structure such as the resins manufactured by The Dow Chemical Company and sold under the DOWEX trademark or the resins made by Rohm and Haas and sold under the Amberlite and Amberlyst trademarks. Preferably, the ion exchange material has a particle size between about 10 mm to about 0.5 mm, particularly, between about 5 mm and about 0.5 mm, and especially between about 4 mm to about 1 mm.

[0028] Suitable inert materials include, without limitation, any inert material that is substantially the same size as the ion exchange material such as inert polymeric resins, inert ceramic materials, glass materials, sands, clays, or the like. Preferred inert materials include, without limitation, the unsulfonated resins.

#### **TECHNOLOGY DESCRIPTION**

[0029] The ion exchange system described below is very similar in construction to many ion exchange systems. However, the present system differs quite significantly in that the resin



contained in the system is diluted with an inert resin (having no functional group or ability to exchange ions stoichiometrically or adsorb ions). Preferred inert materials include: polymeric materials that are not affected by acids or alkalies; or glass. The preferred ion exchange resin comprises 2mm diameter beads composed of polystyrene crosslinked with divinylbenzene and modified with functional groups. The choice of functional groups depends on whether the polymer will be used as a cation exchange resin or an anion exchange resin. The choice will also depend on whether the resin is classified as a weak or strong acid or base.

[0030] The diluent bead are preferably similar in size to the active resin beads, and particularly, substantially the same size as the active resin beads. If the inert material is too small, blockage can occur and if it is too big, channeling can occur. Whether too small or large, the effect is to lower the efficiency of the column. Preferably, the bead size is  $\pm 10\%$  of the size of the active bead size. The column preferably comprises dilution can be from about 15 to about 35%, particularly from about 28 to about 30% being optimum. By using this method the capture rate of ions is greatly increased increasing the ionic capacity of the resin to near its theoretical value. In practice, this means an increase of capacity by about 40%, which is supported by data given herein.

[0031] The Rinse Water Recovery System of this invention comprises three skid-mounted, ion exchange pressure vessels, with interconnecting piping and control valves. The system is configured with one cation exchange column and two anion exchange columns. It is also equipped with a PC-based control system that automates the recycling process. The System of this invention is designed to treat and recover, for reuse, waste waters generated by metal finishing processes.

[0032] Most of the wastewater generated from metal finishing comes from rinsing, which is performed after each process step to remove chemicals. Used rinse water contains dissolved metals and other chemicals that are associated with plating baths. To provide good rinsing and prevent contamination of the plating solutions, recycled water must meet a certain level of purity. The level of purity is often based on two related factors: (1) total dissolved solids and (2) specific conductance. In operation, wastewater from the electroplating line is pumped to the System of this invention and it is processed sequentially through the cation and two anion columns. The treated water is returned to the electroplating line and reused for rinsing. The ion exchange system automatically regenerates itself when the ion exchange columns are exhausted.

#### **PERFORMANCE**

[0033] The system of this invention was evaluated with respect to key operating and performance

criteria. The results of these analyses are summarized below.

#### **System Operation**

[0034] The system of this invention was operated for 15 days for an average duration of 9.2 hours/day. The total operating time was 137.5 hours. The total volume of water processed was 472,476 L (124,828 gal). The average flow rate was 73.96 L/min (19.54 gpm). The standard flow rate of this site was 20 L/min. Thus, the flow rate was increased by over about 5 time. Throughout the test period, the System of this invention operated automatically, without any stoppage for maintenance.

#### **Pollutant Removal Efficiency**

[0035] Average pollutant concentrations and removal percentages measured during the test for the System of this invention are shown in Table I. The parameters listed in Table I are regulated under current metal finishing effluent standards [Ref. 1] and/or are found in the proposed Metal Products and Machinery (MP&M) rule [Ref. 2]. The System of this invention removed 99.9 percent or greater of each pollutant parameter found in the treated effluent (influent) above detection limits.

#### **Ability to Meet Metal Finishing and Proposed Target Effluent Levels**

[0036] The results from each set of analytical data were compared to the applicable Metal Finishing (40 CFR 433) and Proposed MP&M limitations (FR Jan. 3, 2001) to determine if the System of this invention achieved these standards. Sampling was performed on four separate operating days. The Metal Finishing limitations and proposed MP&M limitations were met for all parameters for each day sampling was conducted as shown in Table I.

**Table I**  
**Averaged Pollutant Concentrations and Removal Percentages for the System**  
**Reusability of Treated Wastewater**

Parameter	Average IX Influent mg/L	Average IX Effluent mg/L	Average % Removal	Effluent Meets Metal Finishing and MP&M Standards
Sulphide	Nd	Nd	-	-
O&G (HEM)	Nd	Nd	-	-
TOC	5.5	Nd	100	Yes
Cadmium	Nd	Nd	-	-
Chromium (T)	3.23	< 0.01	99.9	Yes
Chromium (6+)	3.92	Nd	100	Yes
Copper	0.362	Nd	100	Yes
Lead	0.147	Nd	100	Yes

Parameter	Average IX Influent mg/L	Average IX Effluent mg/L	Average % Removal	Effluent Meets Metal Finishing and MP&M Standards
Manganese	Nd	Nd	-	-
Molybdenum	0.501	Nd	100	Yes
Nickel	15.6	0.01	99.9	Yes
Silver	Nd	Nd	-	-
Tin	0.023	Nd	100	Yes
Zinc	0.55	nd	100	yes

\*Percent removals are only calculated for pollutants found above detection limits in the raw or influent wastewater.

[0037] The reusability of the treated wastewater from the System of this invention as process water was determined by comparing the results of the specific conductance and total dissolved solids (TDS) analytical tests of the effluent from this System to standards used by companies in the metal finishing industry for water reuse. Treated water meeting these standards was deemed reusable. In case of water treated by the System of this invention, the Industry standards are: (1) Specific conductance: maximum of 500  $\mu$ S and (2) TDS: maximum of 250 mg/L.

[0038] The System of this invention met the Industry standard water reuse criteria throughout the entire ion exchange cycle. The specific conductance of System effluent samples was measured at or below 10.5  $\mu$ S for operating days 1 to 3 (15 day operating cycle). On day 14, the specific conductance of the system effluent increased to 426  $\mu$ S. The system automatically went into regeneration mode on day 15. It was observed that the company at which the unit was tested reused all water produced by the System of this invention as rinse water on their electroplating line during the test, and that no wastewater was discharged to the city sewer system.

#### **Regeneration**

[0039] The System of this invention is regenerated after the ion exchange resin beds are chemically full. Passing dilute hydrochloric acid through the cation exchange column and dilute sodium hydroxide through the anion columns, and subsequently rinsing the columns with water regenerates the IX columns. The liquid from these steps is collected into a storage tank. The quantities of chemicals used during regeneration were 920 L (243 gal) of concentrated hydrochloric acid and 1,259 L (333 gal) of caustic (50%). These chemicals were diluted with water prior to being used for regeneration. The total volume of wastewater produced during regeneration, including that from rinsing the columns, was 9,690 L (2,560 gal).

#### **Environmental Benefit**

[0040] The environmental benefit of the System of this invention installed at the test site was measured by determining the quantity of regulated pollutants removed beyond the level required

by the current metal finishing regulations (40 CFR 433). The environmental benefit from use of the System of this invention is a reduction of 3,812.4 g (8.4 lbs) of regulated metals for the test period. On an annual basis (260 days/year), assuming 31,498 L (8,322 gal) of wastewater treated per day, the environmental benefit is a reduction of 66,082 g/yr (145.6 lbs/yr) of regulated metal discharged from the test site.

#### **Energy Use**

[0041] The power consumption of the System of this invention is 0.43 kWh/1,000 L (1.63 kWh/1,000 gal.) of wastewater processed. This is used for operating pumps.

#### **Cost of Operation**

[0042] The following parameters were considered in the cost analysis: chemical reagents, electricity, and labor. The cost of treatment for the System of this invention, excluding labor, was \$1.99/1,000 L (\$7.55/1,000 gal.) and \$3.34/1,000 L (\$12.66/1,000 gal.), including labor.

#### **SUMMARY**

[0043] The effluent produced by the System of this invention meets all existing and proposed effluent standards for the metal finishing industry. The removal rate for all regulated parameters found in the test site influent was 99.9% or greater. The effluent from the system had a consistently high quality and it met Industry standard recycle criteria. The non-labor operating cost for the system during the test was \$1.50 /1,000 L (\$5.69/1,000 gal). The cost savings from water/sewer cost reduction at the test site is \$1.72/1,000 L (\$6.50/1,000 gal). Operation of the System of this invention requires approximately 1 hour of labor per day, which is for starting and stopping the system and periodically checking on its progress. No maintenance tasks were performed during the verification test.

#### **DESCRIPTION OF THE TREATMENT SYSTEM**

[0044] Ion exchange is a chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle (*i.e.*, ion exchange resin). Ion exchange reactions are stoichiometric (*i.e.*, predictable based on chemical relationships) and reversible. The strategy employed in using this technology is to exchange substantially harmless ions (*e.g.*, hydrogen and hydroxyl ions), located on the resin, for ions of to be removed from a solution. Generally, these ions are regulated metals.

[0045] In the most basic sense, ion exchange materials are classified as either cationic or anionic. Cation materials such as cation resins exchange hydrogen ions for positively charged ions such as nickel, copper, sodium or the like. Anion material such as anion resins exchange hydroxyl ions for negatively charged ions such as chromates, sulphates, cyanide of the like. Although

different types of ion exchange materials exist, the preferred materials for use in the System of this invention are polymeric resin, in the form of beads.

[0046] Ion exchange resins are usually contained in vessels referred to as columns. The basic column consists of a resin bed, which is retained, in the column via inlet and outlet screens, and service and regeneration flow distributors. Piping and valves are required to direct flow, and instrumentation is required to monitor water quality and control regeneration timing. The systems are operated in cycles including the following four steps: (1) Service (exhaustion) - Water solution containing ions is passed through the ion exchange column or bed until the exchange sites are exhausted; (2) Backwash - The bed is washed (generally with water) in the reverse direction of the service cycle in order to expand and resettle the resin bed; (3) Regeneration - The exchanger is regenerated by passing a dilute solution of the ion originally associated with it (usually a strong mineral acid or base) through the resin bed; and (4) Rinse - Excess regenerant is removed from the exchanger, usually by passing water through it.

[0047] The ion exchange system comprises three skid-mounted, ion exchange pressure vessels, with interconnecting piping and control valves. It is also equipped with a PC-based control system. A schematic diagram of a preferred embodiment of a system of this invention is shown in Figure 1.

[0048] Referring now to Figure 1, the system, generally 100 is shown to include an influent line 102 having a remote controllable shut off valve 104 connected to a source 106 of a metal ion contaminated stream and a water supply line 108 having a remote controllable shut off valve 110 connected to a city water supply 112 (the source of input water) connected to the influent line 102 at a T connector 114. The line 102 includes a pH detector 116 and a conductivity detector 118. The line 102 connects to a remote controllable pump 120, which outputs a pressurized stream into a supply line 122 including a pressure sensor 124, a flow sensor 126 and a remote controllable shut off valve 128. The pressurized stream flowing through the supply line 122 enters an inlet 130 to a cation extraction vessel 132 including a cation extraction bed 134 comprising a volumetric mixture of a cation-exchange resin and a substantially inert resin, where substantially inert means that the resin either does not react at all with the metal ions in the stream or absorbs less than about 1% of any metal ions in the stream. The cation extraction vessel 132 also includes an outlet 136 connected via a first connecting line 138 to an inlet 140 to a first anion extraction vessel 142 including an anion extraction bed 144 comprising a volumetric mixture of an anion-exchange resin and a substantially inert resin, where substantially inert means that the resin either does not react at all with the metal ions in the stream or absorbs

less than about 1% of any metal ions in the stream. The first anion extraction vessel 142 also includes an outlet 146 connected to an inlet 148 via a second connecting line 150 to a second anion extraction vessel 152 including an anion extraction bed 154 comprising a volumetric mixture of an anion-exchange resin and a substantially inert resin, where substantially inert means that the resin either does not react at all with the metal ions in the stream or absorbs less than about 1% of any metal ions in the stream. The second anion extraction vessel 152 also includes an outlet 156 connected to a remote controllable valve 158 via an effluent line 160 which either connects to a sewer inlet or is connects to an inlet to the application from which the metal ion contaminated stream originated.

[0049] The system 100 also includes a regeneration system 162, which is shown in grey. The regeneration system 162 includes an acid regenerant tank 164 containing a regenerant for the cation exchange resin connected to the cation exchange vessel 132 via an acid regenerant supply line 166. The regeneration system 162 also includes an anion regenerant vessel 168 containing a regenerant for the anion exchange resin connected to the first and second anion exchange vessels 142 and 152 via anion regenerant supply lines 170 and 172. Waste streams formed during regeneration are forwarded via waste lines 174, 176 and 178 to a waste storage tank 180 for further processing such as reduction to zero valent metal.

[0050] The system operates by receiving influent from a tank, via a three-way valve and the suction side of a pump. The water is then discharged from the pump under pressure, and is monitored for pH, specific conductance, pressure, and flow. The resultant analogue signals are sent to the programmable logic controller (PLC) for subsequent processing and display. Each of the analogue signals has two high-level and two low-level alarms. The alarms cause the valve systems to either open or close, which cause a change of direction or stopping of flow. The water is allowed to enter the top of the first vessel containing a cation resin to remove the initial shock loading of heavy metals, whereupon it exits at the vessel.

[0051] The partially de-ionized water then enters the second and third vessels (anion columns) in the same manner as the first vessel, and there the remaining ionic loading is removed. The resultant discharge from the third vessel is again monitored for pH and specific conductance and can then be reused in the metal finishing process. The contaminants from the influent (*i.e.*, cations such as metals and anions such as hexavalent chromium and nonmetals) will remain in each of the three vessels bonded to each of the special purpose resins. The water is allowed to flow continuously through the system until such time that the resin is exhausted (*i.e.*, its ability to remove cations and anions from the water is ended). This is determined by the specific

conductance of the water exiting the system at the third vessel. At this point, the system will go off line (usually outside production hours) and regenerate itself *in situ*.

[0052] Regeneration consists of four stages: (1) backwash, DI water at 106 – 114 L/min (28 – 30 gpm); (2) chemical injection, chemicals diluted with DI water at 11 – 15 L/min (3– 4 gpm); (3) slow rinse, DI water at 11 – 15 L/min (3 – 4 gpm); and (4) fast rinse, DI water at 106 – 114 L/min (28 – 30 gpm).

[0053] The ion exchange regeneration process is carried out automatically. Each vessel will regenerate itself in turn starting with the first vessel. Passing acids and/or bases over the resins, which will remove the captured cations and anions, carries out regeneration of the resin. City water is used as a rinse following regeneration. This regenerant will exit each of the vessels and be captured in the regenerant storage for subsequent processing and disposal. At this point, the unit will then be ready to go back on line for the processing of influent.

#### Test Site Installation

[0054] The System of this invention was tested at a test site in Houston, Texas. It is a metal finishing job shop that performs nickel and chromium electroplating, electroless nickel plating, and passivation using nitric acid. The System of this invention that was installed at the test site is rated at a maximum flow of 114 L/min (30 gpm). It has one cation column (1.02 m<sup>3</sup> of resin) and two anion columns (total of 1.13 m<sup>3</sup> of resin). The majority of wastewater generated at the test site is rinse water and to a lesser extent spent cleaning and plating baths. Prior to installation of the closed-loop system, an average of 3,400 L/day (898 gal) of wastewater was discharged to the city sewer. The quantity of regulated metals (mostly nickel and chromium) entering the wastewater is typically 12.5 kg/day (27.6 lbs/day).

[0055] During operation, the raw wastewater is pumped from the equalization tank to the System of this invention, and the effluent is discharged to the final storage tank, from where it is available for reuse on the metal finishing line. In this mode, the System of this invention is operated continuously during production hours and is idled during non-production hours. The system is operated in this manner until the resin columns require regeneration, which occurs approximately every 10 to 20-production days, depending on chemical loading. The system treats wastewater until the resin is exhausted. The point of exhaustion is determined by the specific conductance of the water exiting the system at vessel number 3. Once the resin is exhausted, the system goes off line (usually outside of production hours) and regenerates itself *in situ*. Regenerant is collected in the regenerant storage tank. Figure 2 shows test points.

[0056] Referring now to Figure 2, another preferred embodiment of a system of this invention,

generally 200, is shown to include an equalization tank 202 which receives metal ion containing aqueous solution derived from an industrial application such as a metal plating application. A stream from the tank 202 is forwarded via a feed line 204, which includes a first sampling port 206a and a first detector system 208a including a pH detector, a conductivity detector and a pressure detector, to a cation exchange column 210. The stream is then forwarded from the cation exchange column 210 via a first connecting line 212 to a first anion exchange column 214. The stream is then forwarded from the first anion exchange column 214 via a second connecting line 216 to a second anion exchange column 218. Finally, the stream is forwarded from the second anion exchange column 218 via a third connecting line 220, which includes a second sampling port 206b and a second detector system 208b including a pH detector, a conductivity detector and a pressure detector, to a final storage vessel 222, where the cleaned stream can be disposed of or recycled to the industrial application water intake via an effluent line 224. The cleaned stream meets or exceeds current Federal and State clean water standards.

[0057] Like the system 100, the system 200 also includes a regeneration system 230, which is also shown in grey. The regeneration system 230 includes an acid supply tank 232, containing a strong acid for regenerating the cation exchange resin, connected to the cation exchange column 210 via an acid supply line 234. The regeneration system 230 also includes a caustic supply vessel 236, containing a caustic solution for regenerating the anion exchange resin, connected to the first and second anion exchange columns 214 and 218 via caustic supply lines 238 and 240. Waste streams formed during regeneration are forwarded via waste lines 242, 244 and 246 to a waste storage tank 248 for further processing such as reduction to zero valent metal.

## **METHODS AND PROCEDURES**

### **Test Objectives**

[0058] The test objective includes: (1) To evaluate the ability of the System of this invention to remove pollutants from metal finishing job shop wastewaters, with the metal finishing effluent guidelines and proposed MP&M limits used as target effluent concentrations; (2) To determine the ability of the system to recover water for reuse in the electroplating process; and (3) To evaluate the operating characteristics of the system with respect to energy use, regenerant production and operating costs, and (4) evaluate the environmental benefit by determining the reduction in metals discharged to the city sewer system.

[0059] The following is a summary of primary project objectives. Under normal system operation for the installation at the test site, and processing actual wastewater: (1) Determine the ability of the System of this invention to remove specific contaminants from metal finishing



wastewater and meet target effluent standards and Industry standard criteria for water reuse; (2) Determine the quantity and chemical characteristics of the regenerant produced by the System of this invention; (3) Determine the cost of operating the System of this invention for the specific conditions encountered during testing; and (4) Quantify the environmental benefit by determining the reduction in metals discharged to the sewer system beyond that required by existing metal finishing standards.

### **Test Procedure**

#### **System Set-Up**

[0060] The rinse water system was set up in a closed-loop configuration as shown in Figure 2. Raw wastewater from the plating line was pumped from the feed tank to the ion exchange system. The treated water was returned to the electroplating line and used as rinse water. The system was operated in this configuration for one week prior to testing. The ion exchange system was regenerated prior to testing and the regenerant and effluent storage tanks were drained.

#### **Testing**

[0061] During testing, the ion exchange system was operated during production hours (i.e., approximately 0600 hrs to 1600 hrs, five days per week) and idled during off hours. During the test, the system was operated for one full ion exchange cycle which lasted 15 days (137.5 operating hours). A total of 472,467 L (124,828 gal) of wastewater was processed during the test. Regeneration of the ion exchange columns was automatically initiated when the specific conductivity of the effluent approached 500  $\mu$ S. Sampling of the System of this invention influent and effluent was conducted during four separate days; the first three days of the operating cycle and the 14<sup>th</sup> day of the cycle. Day 14 sampling was performed in order to evaluate the characteristics of the effluent one-day prior to regeneration.

#### **Sample Collection and Handling**

[0062] Samples were collected from the seven sampling points identified in Figure 2. The procedures used at each sampling point are described below.

##### **Ion Exchange System Influent (sample point 5)**

[0063] Grab samples of influent to the ion exchange system were collected from a discharge line for hexavalent chromium, other metals, pH, TDS, and specific conductance analyses.

##### **Ion exchange system effluent (sample point 6)**

[0064] Grab samples of treated wastewater from the ion exchange polishing system were collected from a sampling port for hexavalent chromium, other metals, pH, TDS, specific conductance, O&G, and sulphide analyses.

### **Ion exchange system regenerant (sample point 7)**

[0065] The ion exchange system is regenerated approximately every 20 operating days. The regenerant is collected in a storage tank. At the time of sampling, each sample container was labeled with the date, time, and sample identification (ID) number. Samples were temporarily stored on-site in coolers containing ice. The samples were transported to a local laboratory for analysis. A chain of custody (COC) form accompanied the samples. The COC form provided the following information: project name, project address, sampler's name, sample numbers, date/time samples were collected, matrix, required analyses, and appropriate COC signatures.

### **Sample Methods And Data Handling And Comparison**

**Table II,  
Sample Quantities from Each Sampling Point**

Sample Location/Parameters	Bottle Type	Day 1	Day 2	Day 3	Day 4	Total Sample
Ion Exchange Influent (Sample point 5)						
TOC	125 mL amber glass bottle (4 each)	1	1	1	1	4
Cr <sup>6+</sup> , TSS, TDS, pH, specific conductance	500 mL plastic bottle	1	1	1	1	4
Metals*	500 mL plastic bottle	1	1	1	1	4
O&G (HEM)	1,000 mL wide mouth glass jar (2 each)	1	1	1	1	4
Sulfide	250 mL plastic bottle	1	1	1	1	4
Final Treated Wastewater (Sample point 6)						
TOC	125 mL amber glass bottle (4 each)	1	1	1	3**	6
Cr <sup>6+</sup> , TSS, TDS, pH, specific conductance	500 mL plastic bottle	1	1	1	3**	6
Metals*	500 mL plastic bottle	1	1	1	3**	6
O&G (HEM)	1,000 mL wide mouth glass jar (2 each)	1	1	1	3**	6
Sulfide	250 mL plastic bottle	1	1	1	3**	6
Regenerant (Sample point 7)						
Cr <sup>6+</sup>	500 mL plastic bottle	-	-	-	1	1
Metals*	500 mL plastic bottle	-	-	-	1	1

\*Cadmium, chromium (T), copper, iron, lead, manganese, molybdenum, nickel, tin, and zinc

\*\*Includes duplicate and matrix spike

### **Ion Exchange System Operational Data**

[0066] Data from the internal logging system of the ion exchange unit will be used to provide operational data (non-critical). The system has the following parameters monitored and continuously logged to disk: (1) Inlet specific conductance ( $\mu$ S); (2) pH; (3) Pump discharge pressure (psi); (4) Flow (gpm); and (5) Outlet specific conductance ( $\mu$ S).

Prior to testing, the measurement devices will be calibrated according to each manufacturer's procedures. All events are date and time stamped.

#### Analytical Procedures

[0067] All analytical procedures that have been used during this test are EPA methods or other recognized methods. A summary of analytical tests is presented in Table III

Table III  
Summary of Analytical Tests and Requirements

Parameter	Test Method	Preservation/Handling	Hold Time
Metals (dissolved)	EPA 200.7	Cool storage (<4°C) pH <2 w/HNO <sub>3</sub>	6 months
Metals (sludge)	SW-846 3050B/6010B	cool storage (<4°C)	6 months
Chromium (hexavalent)	SW-846 7196A	cool storage (<4°C)	24 hrs
O&G (as HEM)	EPA Method 1664	cool storage (<4°C) pH <2 w/HNO <sub>3</sub>	28 days
pH	digital meter	NA	analyze immediately
sulfide (S)	EPA Method 376.2	cool storage (<4°C) zinc acetate + NaOH to pH >12	7 days
TDS	EPA Method 160.1	cool storage (<4°C)	7 days
TOC	EPA Method 415.1	cool storage (<4°C) acidify to pH <2 w/HNO <sub>3</sub>	28 days
TSS	EPA Method 160.2	cool storage (<4°C)	7 days
specific conductance	EPA Method 120.1	cool storage (<4°C)	28 days
sludge % water	SW-846 Draft Update IVA 9000	cool storage (<4°C)	28 days
sludge specific gravity	SM2710F	cool storage (<4°C)	28 days

#### Ability to Meet Metal Finishing and Proposed MP&M Limitations

[0068] The results of each test cycle will be compared to the applicable metal finishing limitations (table IV) and Proposed MP&M limitations (table V). To meet a metal finishing or MP&M limit, the analytical result must be equal to or below the corresponding daily maximum limit. The comparison will be made on a parameter-by-parameter basis for each cycle. The applicable limitations are the pretreatment standards for existing sources for the metal finishing category (40 CFR 433.15) and proposed pretreatment standards for existing sources for the MP&M Job Shop subcategory (66 FR 424).

**Table IV**  
**Applicable Pretreatment Standards for Existing Sources**  
**for the Metal Finishing Category (40 CFR 433.15)**

Parameter	Metal Finishing Category (40 CFR 433.15)	
	Daily Max., mg/L	Monthly Avg., mg/L
Cadmium	0.69	0.26
Chromium	2.77	1.71
Copper	3.38	2.07
Lead	0.69	0.43
Nickel	3.98	2.36
Zinc	2.61	1.48

**Table V**  
**Applicable Proposed Pretreatment Standards for Existing Sources**  
**for the MP&M Job Shop Subcategory (66 FR 424)**

Parameter	MP&M Job Shop Subcategory (66 FR 424)	
	Daily Max., mg/L	Monthly Avg., mg/L
Cadmium	0.21	0.09
Chromium	1.3	0.55
Copper	1.3	0.57
Lead	0.12	0.09
Manganese	0.25	0.10
Molybdenum	0.79	0.49
Nickel	1.5	0.64
Tin	1.8	1.4
Zinc	0.35	0.17
O&G (as HEM)	52	26
TOC	78	59
Sulfide (as S)	31	13

#### **Pollutant Removal Efficiency**

[0069] The pollutant removal efficiency is calculated based on a comparison of raw wastewater and treated wastewater concentrations for each pollutant parameter and each run. The equation for zinc removal is shown below. The removal efficiency rate for each pollutant parameter will be separately calculated. These include: O&G (as HEM), TOC, cadmium, hexavalent chromium, chromium (T), copper, lead, manganese, molybdenum, nickel, sulfide (as S), tin, and zinc.

$$Z_{\text{remove}} (\%) = [((Z_i \times V_i) - (Z_e \times V_e)) / (Z_i \times V_i)] \times 100\%$$

where:  $Z_{\text{remove}}$  = zinc recovery efficiency;  $Z_i$  = raw wastewater zinc concentration (mg/L);

$V_i$  = raw wastewater volume processed during the test cycle (L);  $Z_e$  = treated wastewater zinc

concentration (mg/L); and  $V_E$  = treated wastewater volume processed during the test cycle (L).

#### **Reusability of Treated Wastewater**

[0070] The reusability of the treated wastewater as process water will be determined by comparing the results of the pH and specific conductance analytical tests of the final treated water to standards used by the test site for water reuse. Treated water meeting both of these standards will be deemed reusable. The Industry standards are: (1) Specific conductance: maximum of 500  $\mu$ S and (2) pH: within the range of 5.0 to 9.0 standard units.

#### **Energy Usage**

[0071] Will be calculated by summing the total quantity of horsepower (hp) hours for the system and dividing by 1.341 hp-hr/kWh to arrive at electricity needs.

#### **Cost Analysis**

[0072] Cost analyses will be performed. These analyses will determine the operating costs of the System of this invention considering the following cost parameters: chemical reagents, steel plates, other materials (e.g., filters), electricity, labor, and sludge management. Costs will be calculated and expressed in dollars per thousand liters processed (\$/1000 L) by dividing the cost by the total volume of wastewater processed during the verification test. Total costs will be calculated separately for each system by summing the individual cost elements. The calculation of treatment cost is shown below.

$$C_{\text{treat cost}} = (R + A + M + E + L + S) / V$$

where:  $C_{\text{treat cost}}$  = cost of treatment (\$/1000 L); R = cost of chemical reagents used (\$); M = cost of materials used (\$); E = cost of electricity used (\$); L = cost of labor (\$); and V = volume of wastewater processed during the v test (1000 L).

#### **Environmental Benefit**

[0073] This analysis will quantify the environmental benefit of the ion exchange technology installed at the test site by determining the quantity of regulated pollutants removed beyond the level required by the metal finishing regulations (40 CFR 433).

$$P_B = P_V - P_H$$

where:  $P_B$  = quantity of regulated pollutants removed beyond the level required (gram (g)/1000L);  $P_V$  = sum of allowable pollutant discharged (g/1000 L) (calculated by multiplying the daily maximum limit times the volume of wastewater processed and summing over all regulated parameters); and  $P_H$  = sum of actual pollutant mass discharged during verification test (g/1000 L) (calculated by multiplying the average final concentration for the three runs

times the volume of wastewater processed and summing over all regulated parameters)

## Results

**Table VI**  
**Analytical Results for IX Influent and Effluent**

Parameter	IX Influent (sample point 5)					IX Effluent (sample point 6)				
	Day 1	Day 2	Day 3	Day 14	Avg.	Day 1	Day 2	Day 3	Day 14	Avg.
Cadmium, mg/L	ND	ND	ND	ND	<0.005	ND	ND	ND	ND	<0.005
Chromium (T), mg/L	3.43	3.37	6.43	0.044	3.32	ND	ND	ND	0.019	<0.01
Chromium +6, mg/L	3.80	3.57	6.89	1.42	3.92	ND	ND	ND	ND	<0.75
Copper, mg/L	0.262	0.456	0.701	0.030	0.362	ND	ND	ND	ND	<0.010
Iron, mg/L	-	-	-	1.70	1.70	-	-	-	ND	<0.400
Lead, mg/L	0.055	0.201	0.332	ND	0.147	ND	ND	ND	ND	<0.10
Manganese, mg/L	ND	ND	ND	ND	<0.030	ND	ND	ND	ND	<0.030
Molybdenum, mg/L	ND	ND	ND	0.501	<0.13	ND	ND	ND	ND	<0.020
Nickel, mg/L	1.23	1.09	60.0	0.151	15.6	ND	ND	ND	0.045	0.01
Silver, mg/L	ND	ND	ND	ND	<0.010	ND	ND	ND	ND	<0.010
Tin, mg/L	ND	0.037	0.053	ND	<0.023	ND	ND	ND	ND	<0.020
Zinc, mg/L	0.239	0.635	1.09	0.250	0.55	ND	ND	ND	ND	<0.030
Specific Conductance, mS	328	480	1250	1450	877	10.5	10.0	10.5	426	114
Lab pH	3.56	3.35	2.75	2.53	3.05	-	-	-	-	-
Field pH						-	-	-	-	-
TDS, mg/L	134	151	444	200	232	83	100	55	230	117
TSS, mg/L	ND	ND	ND	ND	<10	ND	ND	ND	ND	<10
Sulfide, mg/L	ND	ND	ND	ND	<5	ND	ND	ND	ND	<5
TOC, mg/L	1.28	1.6	8.27	10.9	5.5	ND	ND	ND	ND	<1
O&G, mg/L	ND	ND	ND	ND	<5.6	ND	ND	ND	ND	<5.6

**Table VII**  
**Analytical Results for Ion Exchange Regenerant**

Parameter	Concentration of Parameter in IX Regenerant, mg/L	Mass of Parameter in IX Regenerant, kg (lbs)*
Cadmium	ND	-
Chromium (T)	5,780	56.0 (123.2)
Chromium (+6)	6,040	58.5 (128.7)
Copper	30.7	0.4 (0.9)
Iron	-	-
Lead	ND	-
Manganese	ND	-
Molybdenum	ND	-
Nickel	30,400	294.6 (648.1)
Silver	-	-
Tin	ND	-
Zinc	100	1.0 (2.2)

\*Based on 9,690 L (2,560 gal) of regenerant generated.

**Table VIII**  
**System of this invention Operating Data**

Processing Day	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Avg. for 15 Processing Days
Processing Time, hrs.	9.6	11.1	10.4	10.2	9.6	9.4	8.6	8.8	7.1	10.8	9.3	9.3	9.1	10.4	3.6	9.2
Volume Processed, L (gal.)	28,200 (7,451)	32,302 (8,534)	29,712 (7,850)	29,244 (7,726)	28,593 (7,554)	25,764 (6,807)	24,288 (6,417)	27,205 (7,187)	32,207 (8,509)	42,130 (11,131)	35,629 (9,413)	37,716 (9,965)	37,990 (10,037)	46,015 (12,157)	15,475 (4,089)	31,498 (8,322)
<b>Flow, L/min (gpm)</b>																
Average	48.90 (12.92)	48.30 (12.76)	47.50 (12.55)	47.58 (12.57)	49.58 (13.10)	45.91 (12.13)	46.86 (12.38)	51.25 (13.54)	75.40 (19.92)	64.80 (17.12)	63.97 (16.90)	67.41 (17.81)	69.30 (18.31)	73.96 (19.54)	72.10 (19.05)	58.19 (15.37)
Minimum	37.85 (10.00)	30.28 (8.00)	22.71 (6.00)	30.28 (8.00)	30.28 (8.00)	30.28 (8.00)	37.85 (10.00)	37.85 (10.00)	52.99 (14.00)	52.99 (14.00)	52.99 (14.00)	52.99 (14.00)	56.78 (15.00)	41.64 (11.00)	60.56 (16.00)	41.89 (11.07)
Maximum	113.55 (30.00)	113.55 (30.00)	98.41 (26.00)	113.55 (30.00)	83.27 (22.00)	102.20 (27.00)	83.27 (22.00)	113.55 (30.00)	113.55 (30.00)	113.55 (30.00)	83.27 (22.00)	83.27 (22.00)	83.27 (22.00)	83.27 (22.00)	87.06 (23.00)	97.91 (25.87)
Std. Dev.	8.55 (2.26)	8.06 (2.13)	4.96 (1.31)	5.37 (1.42)	7.65 (2.02)	3.97 (1.05)	0.25 (0.07)	10.33 (2.73)	5.37 (1.42)	4.92 (1.30)	4.05 (1.07)	3.67 (0.97)	3.29 (0.87)	4.28 (1.13)	4.35 (1.05)	5.27 (1.39)
<b>Inlet pH</b>																
Average	4.47	3.68	3.25	4.34	3.99	3.88	3.01	3.40	3.41	3.13	3.25	3.25	2.95	2.80	2.72	3.44
Minimum	3.22	2.78	2.79	3.11	2.97	2.29	2.74	3.14	3.13	2.77	3.06	2.97	2.76	2.70	2.59	2.87
Maximum	9.31	10.34	7.86	11.32	9.54	10.23	4.69	4.94	8.66	6.21	4.50	4.76	4.61	4.30	4.13	7.03
Std. Dev.	1.59	1.77	0.96	2.05	1.78	1.85	0.36	0.26	0.37	0.33	0.20	0.30	0.26	0.21	0.28	0.84
<b>Inlet Conductivity, <math>\mu</math>S</b>																
Average	240	640	710	580	320	910	770	290	230	480	240	360	930	1,410	2,230	689
Minimum	0	100	100	100	0	0	0	0	0	0	0	0	0	0	0	20
Maximum	1,000	1,200	1,200	7,400	700	5,700	1,200	500	800	1,800	500	500	1,300	1,700	3,400	1,927
Std. Dev.	130	260	300	1,090	140	1,240	290	100	90	300	80	120	270	270	610	353
<b>Outlet Conductivity, <math>\mu</math>S</b>																
Average	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.220	0.00	0.00	0.08	0.00	0.40	222.28	410.00	42.18
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	405.00	27.00
Maximum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	416.00	438.00	57.20
Std. Dev.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.27	0.05	0.49	203.90	2.06	13.79

Total processing time for 15 days was 137.5 hrs. Total volume of water processed was 472,474 L (124,828 gal.).



[0074] Unit cost data for labor, electricity, and IX system regeneration chemicals are shown in Table IX. The test site provided this information.

**Table IX**  
**Unit Cost Data**

Parameter	Cost
IX System Labor	\$20/hr. (loaded rate, includes overhead and fringe benefits)
Electricity	\$0.10/kWh
Water/Sewer	\$6.50/1,000 gal.
Hydrochloric Acid	\$0.28/L
Sodium Hydroxide	\$0.38/ L

[0075] Chemical usage during the ETV test are shown in Table X.

**Table X**  
**Chemical Usage Data**

Item	Usage
Hydrochloric Acid Used*	238 gal
Sodium Hydroxide Used*	305 gal

\*For entire ion exchange cycle (472,475 L treated).

[0076] The labor required to operate the ion exchange system was needed for starting and stopping the system on a daily basis and periodically checking on its progress. The average labor needed per day was 1.0 hours. At the completion of the ion exchange cycle, the system was regenerated. The regeneration process took 7 hours to complete, although it was mostly performed automatically and unattended. The labor required for regeneration was 1.5 hours (not including treatment of regenerant), which was needed for initiating the regeneration cycle and periodically checking on the progress of regeneration.

## **EVALUATION OF RESULTS**

### **System Operation**

[0077] A diagram of the test site chromium/nickel electroplating line and rinse water recycle system is shown in Figure 3. The plating line, generally 300, includes five process steps: an alkaline cleaning step 302, an electrocleaning step 304, an acid dip step 306, a nickel electroplating step 308, and a chromium electroplating step 310. Each process step is followed by at least one rinse step. There is a single overflow rinse 312 after the alkaline cleaning step 302. There is two counter flow rinses 314a&b after the electrocleaning step 304. There are two counterflow rinses 316a&b after the acid dip step 306. There are three counterflow rinses 318a-c following the nickel electroplating step 308 and three counterflow rinses 320a-c following the chromium electroplating 310. For those

rinses including more than one rinse step, the rinse steps are interconnected via dashed line. In order for a rinse tank to be effective, the concentration of chemicals in the rinse tank must be sufficiently low. In a counterflow rinse system, such as those used at the test site, it is the final rinse of each rinse system that is of particular concern. If the concentration of chemicals in the final rinse is too high, then chemicals remain on the parts. This can cause unwanted chemical reactions, staining of parts, and contamination of subsequent process tanks.

[0078] Prior to the installation of the Rinse Water recovery System 322 of this invention, used rinse water was stored in a large equalization tank (18,925 L), treated using a metals precipitation technology (electrocoagulation), and discharged to the city sewer. The average volume of wastewater discharged was 4000 gpd. According to the test site, production rates and pollutant loading rates were approximately the same before and after the closed-loop rinse system was installed.

[0079] During the course of the test, the test site electroplating rinse water system 322 was operated in a closed-loop and configured similar to the apparatus of Figures 1-2. The system 322 also included two storage tanks 324a&b and two pumps 326a&b. Used rinse water from the rinse tanks, shown in solid black lines, was processed through the System of this invention and returned to the rinse tanks via grey lines. No wastewater was discharged to the city sewer system during the 15 operating day duration of the test. Rinse water was recycled by the System of this invention at an average rate of 58.19 L/min (15.37 gpm) for an average duration of 9.2 hrs/day. The average daily volume of water recycled was 32,121 L/day (8,484 gpd).

[0080] Table XI compares the concentration of chemicals in the used rinse water, before and after implementation of closed-loop rinsing at the test site. The average concentration of total dissolved solids (TDS) in the used rinse water prior to implementation of closed-loop rinsing was 1,320 mg/l. Following implementation of closed-loop rinsing, the TDS concentration was 232 mg/l, a 569% decrease. This comparison indicates that the water in the rinse tanks was significantly cleaner with the new closed-loop system than with the old, non-circulated system. This is due to the higher flow rate of water used in the closed-loop system as compared to the non-circulated system.

[0081] The mass of TDS discharged from the rinse systems was similar before and after implementation of closed-loop rinsing (9,900 g/day before compared to 7,308 g/day after closed-loop rinsing was implemented). However, the mass of chromium and nickel discharged from the rinse systems dropped significantly after closed-loop rinsing was implemented. Test site personnel attributed this drop to use of recovery rinsing, which they implemented simultaneously along with closed-loop rinsing. Prior to closed-loop rinsing, The test site was hesitant to use recovery rinsing

due to a fear of building up contaminants in process tanks. This can occur when rinse water is insufficiently pure enough to effectively remove chemicals from the parts and the chemicals from one process tank are carried over to a subsequent process tank.

**Table XI**  
**Impact of Closed-Loop Ion Exchange System Installation**

Parameter	Concentration of Parameter in Used Rinse Water Prior to Closed-Loop Installation, Avg.	Mass of Parameter in Used Rinse Water Prior to Closed-Loop Installation, Avg.	Concentration of Parameter in Used Rinse Water After Closed-Loop System Installation, Avg.	Mass of Parameter in Used Rinse Water After Closed-Loop System Installation, Avg.
Cadmium	0.008 mg/l	0.06	<0.005 mg/l	<0.2
Chromium (T)	89.5 mg/l	671	3.32 mg/l	105
Chromium +6	70.5 mg/l	529	3.92 mg/l	123
Copper	1.31 mg/l	9.8	0.362 mg/l	11.4
Lead	0.252 mg/l	1.9	0.147 mg/l	4.6
Manganese	0.171 mg/l	1.3	<0.030 mg/l	<1.0
Nickel	202 mg/l	1,515	15.6 mg/l	491
Tin	0.57 mg/l	4.3	<0.023 mg/l	<1.0
Zinc	3.09 mg/l	23.2	0.55 mg/l	17.3
TDS	1,320 mg/l	9,900	232 mg/l	7,308

[0082] A graph showing specific conductivity data, logged by the Lobo Liquids data acquisition system, over the entire course of the test is shown in Figure 4. This graph indicates that the System of this invention produced a consistently pure effluent throughout the entire ion exchange cycle, until resin bed was nearly exhausted (chemically full). The point at which the specific conductivity rapidly rises is termed "breakthrough." This occurred 128.4 hours into the IX cycle. Just prior to breakthrough, the specific conductivity was 4 mS. Within 10 seconds, the specific conductivity increased to 410 mS. The specific conductivity stayed in the range of 408 mS to 438 mS for the remainder of the IX cycle, a time period of 9.1 operating hours. Regeneration was automatically initiated at that point in time.

#### **Pollutant Removal Efficiency**

[0083] The pollutant removal efficiency was calculated based on a comparison of influent and effluent concentrations for each pollutant parameter. Removal efficiency was only calculated for parameters that were found at concentrations above detection limits in the influent for at least one day. These calculations are performed for paired sets of analytical results (i.e., daily influent and effluent samples). Also, average removal efficiencies were calculated for the entire test. For the purpose of pollutant removal calculations, parameters that were not detected in the treated wastewater by analytical measurements were given a concentration value of zero.

[0084] The results of the pollutant removal efficiency analysis for the System of this invention are

shown in Table XII. Percent removal could not be calculated for cadmium, manganese, silver, and sulphide because the concentration of these parameters in the influent was below detection limits for all four days batches. Average pollutant percent removals for the remaining parameters ranged from 99.9 percent to 100.0 percent.

**Table XII**  
**Results of Pollutant Removal Efficiency Analysis Lobo System**

Parameter	IX Inf. Day 1 mg/L	IX Eff. Day 1 mg/L	% Removal Day 1	IX Inf. Day 2 mg/L	IX Eff. Day 2 mg/L	% Removal Day 2	IX Inf. Day 3 mg/L	IX Eff. Day 3 mg/L	% Removal Day 3	IX Inf. Day 14 mg/L	IX Eff. Day 14 mg/L	% Removal Day 14	Avg. for Four Days, % Removal
Cadmium, mg/L	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-	-
Chromium (T), mg/L	3.43	ND	100.0%	3.37	ND	100.0%	6.43	ND	100.0%	0.044	0.019	56.8%	99.9%
Chromium +6, mg/L	3.80	ND	100.0%	3.57	ND	100.0%	6.89	ND	100.0%	1.42	ND	100.0%	100.0%
Copper, mg/L	0.262	ND	100.0%	0.456	ND	100.0%	0.701	ND	100.0%	0.030	ND	100.0%	100.0%
Iron, mg/L	-	-	-	-	-	-	-	-	-	1.70	ND	100.0%	100.0%
Lead, mg/L	0.055	ND	100.0%	0.201	ND	100.0%	0.332	ND	100.0%	ND	ND	100.0%	100.0%
Manganese, mg/L	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-	-
Molybdenum, mg/L	ND	ND	-	ND	ND	-	ND	ND	-	0.501	ND	100.0%	100.0%
Nickel, mg/L	1.23	ND	100.0%	1.09	ND	100.0%	60.0	ND	100.0%	0.151	0.045	91.0%	99.9%
Silver, mg/L	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-	-
Tin, mg/L	ND	ND	-	0.037	ND	100.0%	0.053	ND	100.0%	ND	ND	-	100.0%
Zinc, mg/L	0.239	ND	100.0%	0.635	ND	100.0%	1.09	ND	100.0%	0.25	ND	100.0%	100.0%
TOC, mg/L	1.28	ND	100.0%	1.6	ND	100.0%	8.27	ND	100.0%	10.9	ND	100.0%	100.0%
Sulfide, mg/L	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-	-

Average percent removal for four days calculated using average influent and effluent values for the four days (not shown).

**Ability to Meet Metal Finishing and Proposed Target Effluent Levels**

[0085] The results from each day of sampling were compared to the applicable metal finishing limitations and target level effluent limitations. To meet a metal finishing or target limit, the analytical result must be equal to or below the corresponding daily maximum value. The applicable limitations are the pretreatment standards for existing sources for the metal finishing category (40 CFR 433.15) and proposed pretreatment standards for existing sources for the MP&M Job Shop subcategory (Fed Reg. Jan. 3, 2001, pp. 543-544).

[0086] The results of the comparison for the System of this invention are shown in Table 7. The metal finishing limitations and proposed MP&M limitations were met for all parameters for each day of sampling.

**Table XIII**  
**Results of Regulatory Limits Comparison Analysis for System of this invention**

Parameter	Metal Finishing Category Limits, Daily Max. mg/L	MP&M Job Shop Subcategory Limits, Daily Max. mg/L	Day 1			Day 2			Day 3			Day 14		
			IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No	IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No	IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No	IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No	IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No	IX Eff. Meets Metal Finishing Limits Yes/No	IX Eff. Discharge Meets MP&M Limits Yes/No
Sulfide	NR	31	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
O & G (HEM)	NR	52	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
TOC	NR	78	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cadmium	0.69	0.21	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Chromium	2.77	1.3	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Copper	3.38	0.55	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Lead	0.69	0.12	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Manganese	NR	0.25	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Molybdenum	NR	0.79	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Nickel	3.98	1.5	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Silver	0.43	0.15	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Tin	NR	1.8	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Zinc	2.61	0.35	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

NR = not regulated

### Reusability of Treated Wastewater

[0087] The reusability of the treated wastewater as process water was determined by comparing the results of the specific conductance and TDS analytical tests of the final treated water (System of this invention effluent, i.e., sample point 6) to standards used by the test site for water reuse. Treated water meeting these standards was deemed reusable. The test site standards are: (1) Specific conductance: maximum of 500  $\mu$ S and (2) TDS: maximum of 250 mg/L.

[0088] The results of this comparison are shown in Table XIV. For days 1, 2, 3 and 14 the System of this invention met the test site water reuse criteria.

**Table XIV**  
**Comparison of Analytical Results and Gull Industries Water Recycling Criteria**

Parameter	Recycle Criterion	IX Effluent				IX Effluent Meets Criterion Yes/No
		Day 1	Day 2	Day 3	Day 14	
Specific conductance, mS	500	10.5	10.0	10.5	426	Yes (Days 1, 2, 3, 14)
TDS, mg/L	250	83	100	55	230	Yes (Days 1, 2, 3, 14)

[0089] It should be noted that during the period of testing, it was observed that Gull Industries reused the water produced by the System of this invention as rinse water on their decorative chromium electroplating line. No wastewater was discharged to the city sewer system during the 15-day verification test.

### Energy Use

[0090] The energy requirements were calculated separately for the System of this invention. The results of the energy use analysis are presented in Table XV. Electricity use for the System of this invention during the ETV test was 205 kWh, which is equivalent to 0.43 kWh/1,000 L. For pumps, energy use was calculated by summing the total quantity of horsepower (hp) hours for each system and dividing by 1.341 HP-hr/kWh to arrive at electricity needs.

**Table XV**  
**Results of Energy Use Analysis**

Item	Hp-Hr.	Electricity Use kWh	Electricity Use kWh/1,000 L (KWh/1,000 gal)
System of this invention			
Pumps	275	205	0.43 (1.63)
Total System of this invention		205	0.43 (1.63)

### Cost Analysis

[0091] This analysis determines the operating cost of the System of this invention considering the



following cost parameters: chemical reagents, electricity, and labor. Costs are expressed in dollars per thousand liters processed (\$/1000 L) by dividing the cost by the total volume of wastewater processed during the verification test. Total costs are calculated by summing the individual cost elements. The calculation of treatment cost for either system is shown below.

[0092] The results of the operating cost analysis are shown in Table XVI. Operating costs are displayed both, with and without labor costs.

**Table XVI**  
**Results of Cost Analysis**

Cost Parameter	Unit Cost	Units Used During ETV Test	Cost During ETV Test Batches 1 to 3	Normalized Cost, \$/1,000 L (\$/1,000 gal.)
Sodium Hydroxide	\$0.38/L (\$1.44/gal.)	1,154 L (305 gal.)	\$438.52	\$0.93 (\$3.51)
Hydrochloric Acid	\$0.28/L (\$1.06/gal.)	901 L (238 gal.)	\$252.28	\$0.53 (\$2.02)
Electricity	\$0.10/kWh	205 kWh	\$20.50	\$0.04 (\$0.16)
Total System of this invention, except labor			\$711.30	\$1.50 (\$5.69)
Labor	\$20/hr.	17 hrs.	\$340.00	\$0.72 (\$2.73)
Total System of this invention, including labor			\$1,051.30	\$2.22 (\$8.42)

[0093] Use of the Lobo Liquids Rinse Water Recovery System eliminates the discharge of wastewater at the test site, with the exception of processed regenerant. The cost of water/sewer at this facility is \$1.72/1,000 L (\$6.50/1,000 gal). The water/sewer savings achieved by recovering and recycling water during the test was \$794.74, which is greater than the non-labor operating cost. Although not quantified during this test, the savings would actually be higher since Gull Industries previously used deionized water for rinsing. The cost savings from eliminating the old deionizing system are not included.

#### **Regenerant Analysis**

[0094] The volume of regenerant produced by the System of this invention was measured at the end of the test. The volume was 9,690 L (2,560 gal). The laboratory analyzed a representative sample of the regenerant. Results from measurements and analytical tests are summarized in Table 3.

[0095] At the test site, the regenerant is processed by a metals precipitation technology that is not part of the System of this invention evaluated during this test. The treated regenerant is discharged to the city sewer and the precipitated solids are sent off-site for disposal.

**Environmental Benefit**

[0096] This analysis quantifies the environmental benefit of the System of this invention installed at the test site by determining the quantity of regulated pollutants removed beyond the level required by the metal finishing regulations (40 CFR 433). The results of the analysis are shown in Table 2. Cadmium and silver were not found in the influent and therefore were not included in this analysis. The raw wastewater concentration for copper, lead and zinc were below the values for metal finishing limitations and therefore the raw wastewater concentration was used in calculating environmental benefit for these three parameters.

**Table 2**  
**Results of Environmental Benefit Analysis**

Parameter	Metal Finishing Limitations		Lobo Liquids Influent (Days 1, 2, 3, 14)		Lobo Liquids Effluent (Days 1, 2, 3, 14)		Environmental Benefit, g*
	Avg. Daily Max., mg/L	Allowable Mass Discharge, g*	Avg. Conc., mg/L	Avg. Mass Discharge, g*	Avg. Conc., mg/L	Avg. Mass Discharge, g*	
Cadmium	0.69	326.0	0.0	0.0	0.0	0.0	-
Chromium	2.77	1,308.8	4.410	2,083.6	0.0	0.004	1,308.8
Copper	3.38	1,597.0	0.473	223.5	0.0	0.0	223.5
Lead	0.69	326.0	0.196	92.6	0.0	0.0	92.6
Nickel	3.98	1,880.4	20.8	9,827.5	0.0	0.01	1,880.4
Silver	0.43	203.2	0.0	0.0	0.0	0.0	-
Zinc	2.61	1,233.2	0.650	307.1	0.0	0.0	307.1
Total							3,812.42

\* Based on 472,476L (124,828 gal) treated.

[0097] The environmental benefit from use of the System of this invention is a reduction of 3,812.4 g (8.4 lbs) of regulated metals for the 15-day test period. On an annual basis (260 operating days per year), the environmental benefit would be a reduction of 66,082 g (145.6 lbs) of metal discharged.

[0098] All references cited herein are incorporated by reference. While this invention has been described fully and completely, it should be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

### CLAIMS

We claim:

1. A method for removing metal ions from streams contaminated with metal ions including the step of passing the stream through at least one zone comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.
2. The method of claim 1, further comprising the step of passing the stream through a plurality of zones comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.
3. The methods of claims 1-2, wherein the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material.
4. The methods of claims 1-3, wherein the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industry.
5. The methods of claims 1-4, wherein the stream is an aqueous stream including contaminating metal ion and the resulting stream has metal ion concentrations at or below the concentrations dictated by the current clean water standards
6. A method for closed loop circulation of an aqueous stream with concurrent removal of metal ion contaminates contained in the stream, comprising the steps of:
  - directing an aqueous effluent stream from an outlet of an industrial process contaminated with metal ions to an extraction unit including at least one zone or bed comprising a volumetric mixture of an ion exchange material and an a substantially inert material,
  - passing the effluent stream through the zone or bed at a relatively high stream flow rate to produce a cleaned aqueous stream having metal ion concentrations at or below existing clean water standards, and
  - directing the cleaned stream into an inlet of the industrial process.
7. The method of claim 6, wherein the method is either continuous, semi-continuous, or periodic or batch basis.

8. The methods of claims 6-7, further comprising the step of passing the stream through a plurality of zones comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.
9. The methods of claims 6-8, wherein the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material.
10. The methods of claims 6-9, wherein the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industry.
11. An apparatus for removing metal ion contaminants from an effluent stream comprising an extraction unit including an inlet and an outlet and at least one bed or zone comprising a volumetric mixture of an ion exchange resin and an inert material.
12. The apparatus of claim 11, further comprising a pump sufficient to increase the volumetric flow rate of the stream.
13. The apparatuses of claims 11-12, further comprising a plurality of zones comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.
14. The apparatuses of claims 11-13, wherein the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material.
15. The apparatuses of claims 11-14, wherein the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industry.
16. The apparatuses of claims 11-15 wherein the stream is an aqueous stream including contaminating metal ion and the resulting stream has metal ion concentrations at or below the concentrations dictated by the current clean water standards

17. An apparatus for removing metal ion contaminants for a closed loop circulation of aqueous stream, comprising
- an industrial application producing an effluent stream contaminated with metal ions and
- an extraction unit including at least one zone or bed comprising a volumetric mixture of an ion exchange material and from a substantially inert material, where the metal ion contaminants are removed to a desired low level to produce a clean recycle stream and where the industrial application and the extraction unit are connected by an effluent line so that the effluent stream flows from the industrial application into the extraction unit on a continuous, semi-continuous or periodic basis and a recycle line so that the clean recycle stream flows from the extraction unit into the industrial application.
18. The apparatuses of claim 17, further comprising the step of passing the stream through a plurality of zones comprising a volumetric mixture of an ion exchange material and an a substantially inert material at a relatively high stream flow rate.
19. The apparatuses of claims 17-18, wherein the volumetric mixture comprises from about 90 to 50 vol% of an ion exchange material and from about 10 to 50 vol% of an a substantially inert material.
20. The apparatuses of claims 17-19, wherein the flow rate is at least about 1.5 to about 5 times the flow rate of a stream flow rate generally used in the industry.
21. The apparatuses of claims 17-20, wherein the stream is an aqueous stream including contaminating metal ion and the resulting stream has metal ion concentrations at or below the concentrations dictated by the current clean water standards

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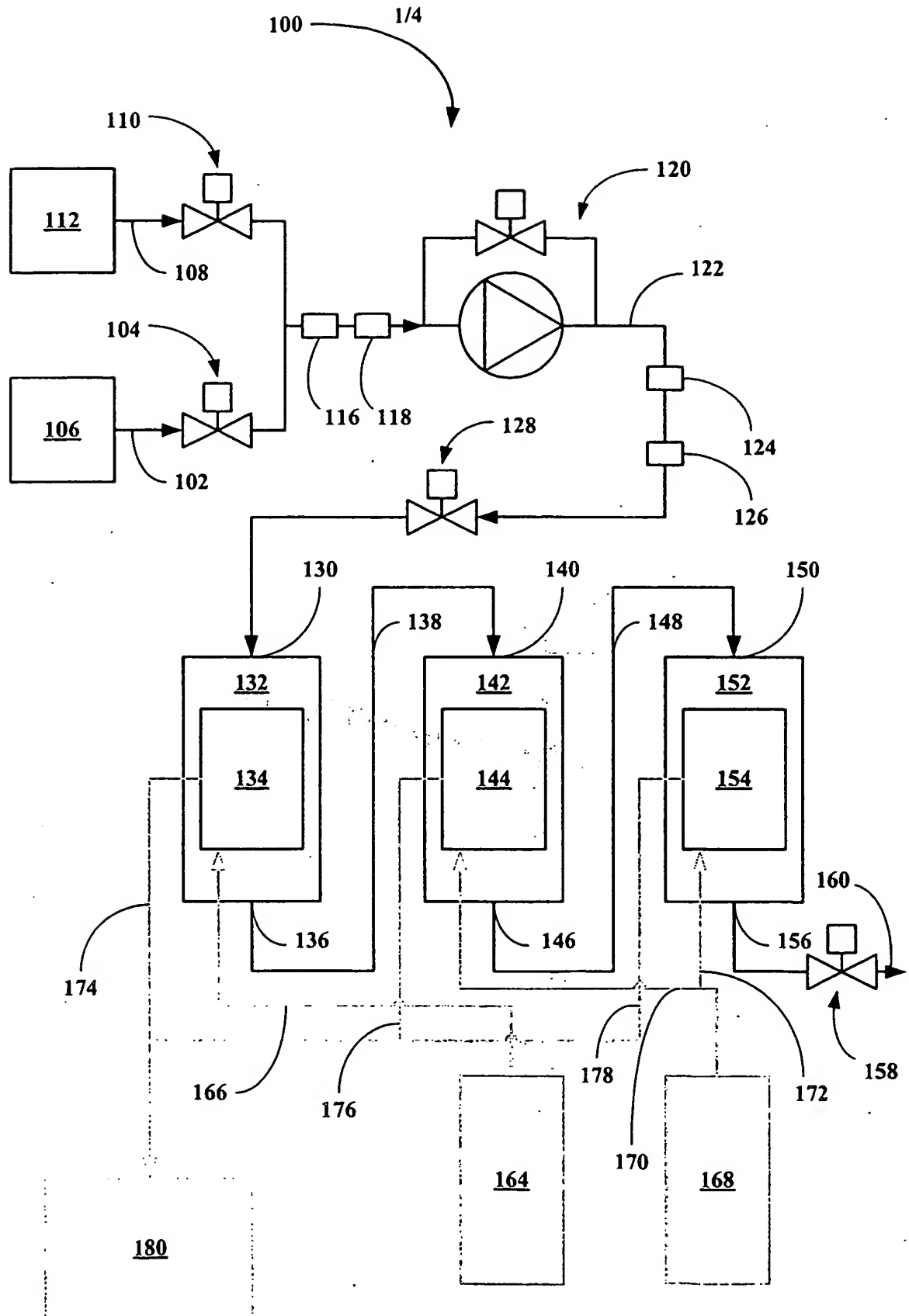


FIG. 1

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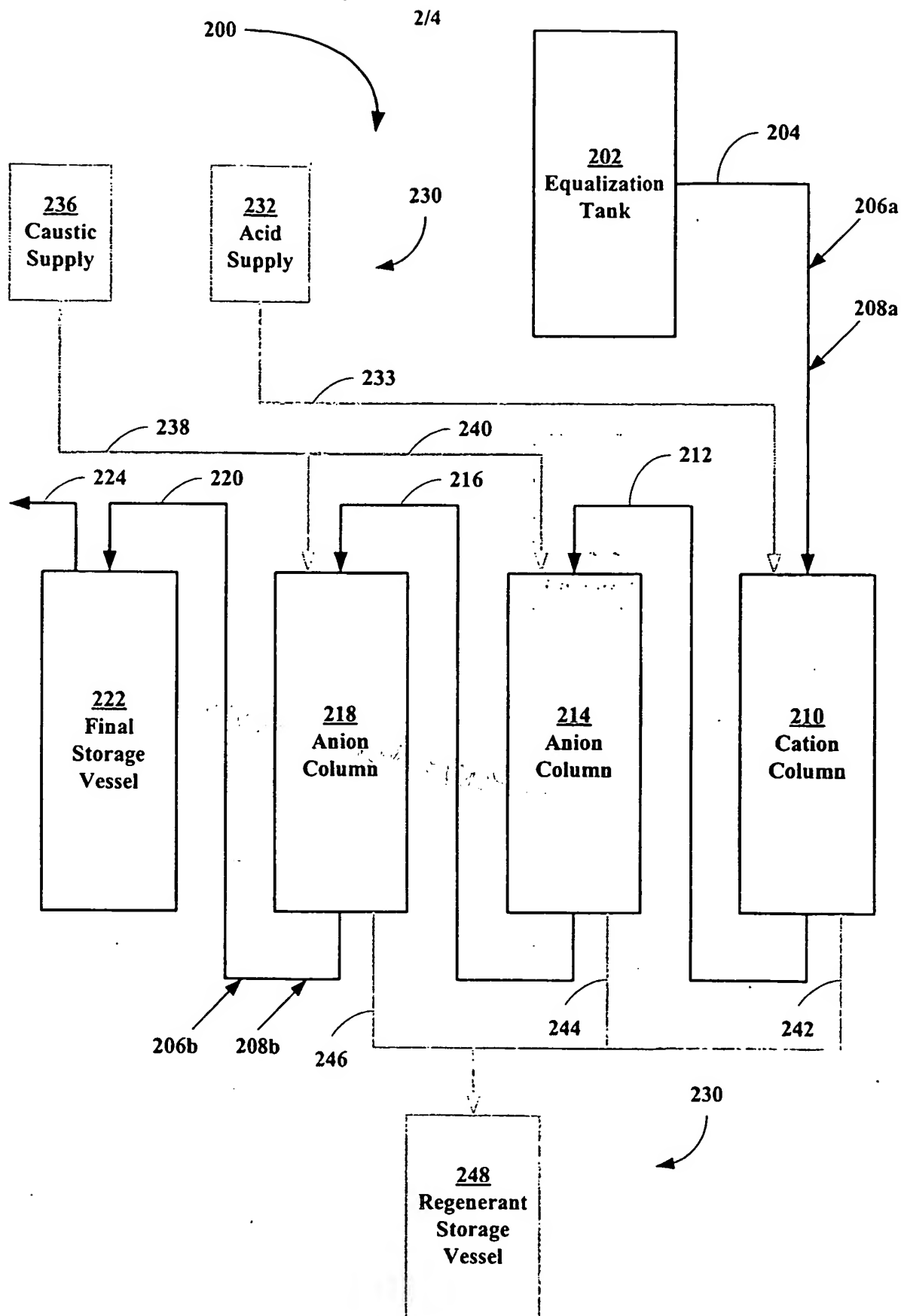


FIG. 2

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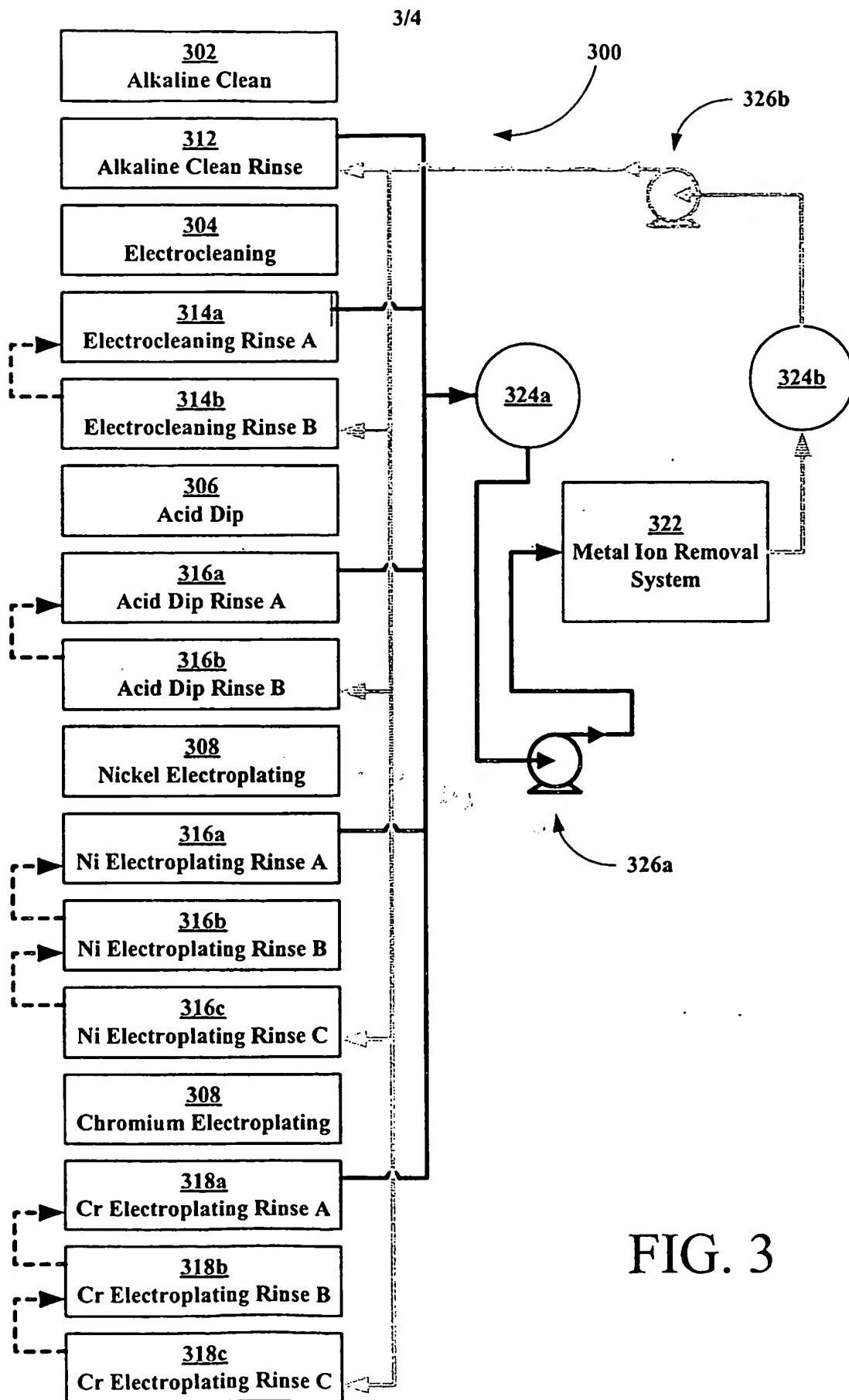


FIG. 3

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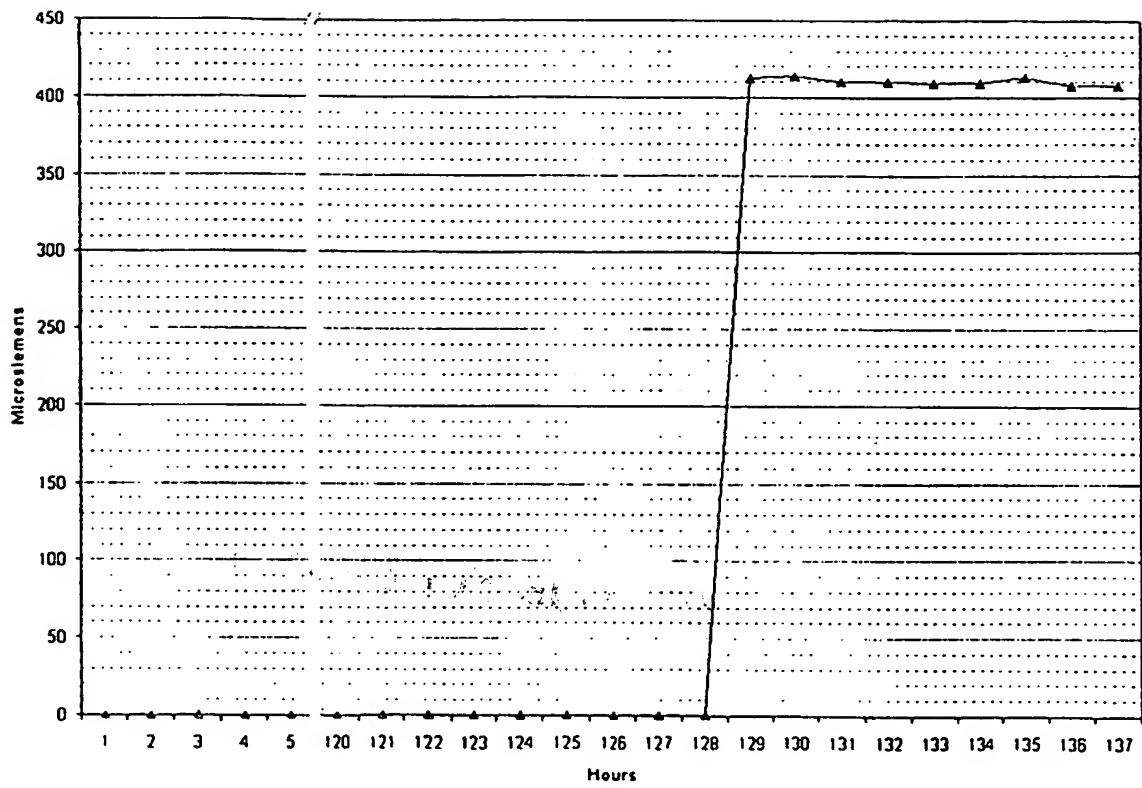


FIG. 4

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